学校编码：10384
学号：20720131150085

分类号_____密级_____
UDC_____

厦门大学

硕 士 学 位 论 文

新型无卤反应型含磷、氮阻燃剂的合成及其阻燃环氧树脂的研究

Synthesis of novel halogen-free reactive flame retardants containing phosphorus and nitrogen, and study on their flame retardant performance on epoxy resins

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论文提交日期：2016 年 05 月
论文答辩日期：2016 年 05 月
学位授予日期：2016 年 月

答辩委员会主席：_____
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2016 年 05 月

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摘要

含 P、N 类化合物用于阻燃环氧树脂因制备简单且高效而受到广泛的关注，但传统的含 P、N 类的阻燃剂，如三聚氰酰氯、三聚氰胺、环三磷腈、和 DOPO 席夫碱基等衍生物的应用，往往会导致固化物 T_g 和机械性能的下降而限制其应用。本文经过分子结构设计，将无卤阻燃元素磷、氮引入到同一分子中，起到高效阻燃环氧并保持其它性能良好的效果。本文主要工作成果如下：

（1）通过一步法将 N-羟乙基苯胺、4-羟基苯甲醛以及 DOPO 反应得到第一种阻燃剂 PNOH，产率 89 %；采用两步法或一步法将 N-苯基-1,4-苯二胺，4-羟基苯甲醛，DOPO 反应得到第二种阻燃剂 PNNO，产率 88 %；采用两步法或一步法将 N-苯基-1,4-苯二胺，对苯二甲醛，DOPO 反应得到第三种阻燃剂 DPN，产率 86.2 %。采用 FTIR、NMR 等手段分别对三种产物的分子结构进行相应的表征，证明成功合成了所设计的目标阻燃剂。

（2）采用不同的测试手段研究了 PNOH 含量对 PNOH/EP 固化物各项性能变化的影响。TGA 结果表明 PNOH/EP 固化物都存在较好的热稳定性且可明显提高残炭率，在氮气氛下残炭率（700 ℃）可达到 31.9 %，而不含 PNOH 的环氧树脂 EP0 为 19.3 %；从 DSC、DMTA 的 T_g 值分析表明，PNOH/EP 固化体系的 T_g 值随 PNOH 的加入而略有下降，这是因为 PNOH 加入会引起交联密度的下降；橡胶态储能模量（E′-190 ℃）、tanδ 值表明，PNOH 的大量加入会减小其交联密度；根据 LOI 以及 UL-94 分析表明，PNOH 的引入可明显提高材料的阻燃性能，燃烧等级达到 V-0 级且不发生滴落，当 PNOH/DDM 的复配比达到 20:80，LOI 值可达 36 %；

（3）对含 DOPO 的席夫碱基化合物 PNNO 对 PNNO/EP 固化物的各项性能影响进行分析。TGA 分析结果表明 PNNO/EP 都具有较好的热稳定性，且可明显提高残炭率；从 DSC、DMTA 的 T_g 值分析表明，PNNO/EP 体系的 T_g 值随 PNNO 加大会有一个先增后减的趋势，这是因为少量 PNNO 的加入能反应完全，固化反应的化学交联与多苯基结构的物理交联共同起作用，会有较高的 T_g 值，但添加量大的时候，反应不完全且会产生部分团聚，使化学和物理交联点减少而减小

交联度；E′-190 ℃、tanδ 也表明 PNNO 大量加入会因反应不充分而减小其交联密度；三点弯曲测试表明，PNNO 的适当引入时，形成 C—O 键比 C—N 的柔性更强而有利于分子链的运动，从而增强材料的韧性，而当 PNNO/DDM 复配比例达一定值后，由于相容性变差而又会降低材料的机械性能；根据 LOI 以及 UL-94 分析表明，PNNO 的引入都可发挥高效阻燃的效果，燃烧等级达到 V-0 级，LOI 值可达 37.1 %。

（4）针对含 DOPO 的席夫碱基化合物 DPN 对 DPN/EP 体系的各项性能改变的影响进行分析。TGA 表明，在氮气氛下，DPN/EP 残炭率可提高到 30.9 %；DSC、DMTA 的 T_g 值表明， DPN/EP 固化体系的 T_g 值与 EP0 都非常的接近，因为 DPN 的分子结构中存在四个活性 N—H 键，与 DDM 的反应活性较为相近，因而会有较高的交联密度；而 E′-190 ℃、tanδ 也说明了 DPN 能较好地参与到环氧的交联固化之中而具有较高的交联密度；LOI 以及 UL-94 分析表明，DPN 的引入也可发挥高效阻燃的效果，燃烧等级达到 V-0 级且不发生滴落，LOI 值可达 41 %。

（5）对比 PNOH/EP、PNNO/EP、DPN/EP 各组分固化物的性能可知，N—H 键比醇羟基或者酚羟基活性更强，当反应官能团活性越高，官能度越大及反应活性越集中，交联度也会更大，且多苯基的线性结构也可增大环氧体系紧密度而保持较高的 T_g 值；C—O 键比 C—N 键的引入更有利于分子链的运动可增强材料的韧性而增大应力，多苯环基的线性刚性结构可增大材料刚性而更好地抵抗外力形变；含 DOPO 的席夫碱基阻燃剂因其高的含 P、N 量以及 DOPO 基团的分布更密集而改善环氧的阻燃性能更佳。

关键词：环氧树脂，阻燃剂，席夫碱基化合物

Abstract

The compounds for epoxy containing P and N have been widely concerned, because of their high efficiency flame retardant properties. However, the application of traditional flame retardants containing P and N, such as the derivatives of cyanuric chloride, melamine,cyclophosphazeneand DOPO-containing Schiff-base groups and so on, often lead to the decrease of the T_g and mechanical properties of the cured products. In this work, based on the molecular design, the halogen-free flame retardant element P and N areintroduced into the same molecular, which have played an efficient flame retardant and maintain good other performances. The main achievements of our work are shown as follows:

(1) The first kind of flame retardant (PNOH) was synthesized via an one-pot procedure among N-Phenyldiethanolamine, 4-hydroxybenzaldehyde and DOPO, with the yield of 89 %. The second kind of flame retardant (PNNO) was synthesized via an one or two pot procedure among N1-phenylbenzene-1,4-diamine, 4-hydroxybenzaldehyde and DOPO, with the yield of 88 %. The third kind of flame retardant (DPN) was synthesized via the same procedure among 4-Amino diphenylamine, Terephthaldicarboxaldehyde and DOPO, with the yield of 86.2 %. The molecular structure of the three products were characterized by FTIR, MS and NMR. It was proved that the designed target flame retardant was successfully synthesized.

(2) Different test analysis methods were used to study the properties of PNOH/EP curing system. TGA results show that PNOH/EP has good thermal stability, and can significantly improves the rate of carbon residue, for example, in the nitrogen, the carbon residue rate (700 ℃) can reach 31.9 %, while the EP0 is 19.3 %. The T_g values obtained from the DMTA and DSC tests show that the T_g values of the PNOH/EP curing system will be slightly decreased with the addition of PNOH, which are due to the decrease of the crosslinking density when the addition ratio of PNOH is high. The

rubber state storage modulus (E-190℃) and the values of tanδ also show that adding large number of PNOH will decrease the crosslinking density. The LOI and UL-94 analysis show that, the introduction of PNOH can significantly improve flame retardant property of materials, with the V-0 grade of UL-94and non-dropping. When the PNOH/DDM compound ratio reaches to 20:80, the LOI value can reach to 36 %.

(3) The influences of the introduction of DOPO-containing Schiff-base flame retardant (PNNO) on the properties of PNNO/EP curing system were analyzed. TGA results show that PNOH/EP has good thermal stability, and can significantly improve the rate of carbon residue. The T_g values obtained from the DMTA and DSC tests show a trend of first increased and then decreased. Because the addition of a small amount of PNNO can react with epoxy completely. Physical crosslinking and chemical crosslinking of the curing reaction work together and make the curing epoxy with a higher T_g values. However, when the amount is large, the reaction is not complete and will produce partial reunion, so that the chemical and physical crosslinking point is reduced and the degree of cross-linking is reduced. The rubber state storage modulus (E-190℃) and the values of tanδ also show that a higher proportion of PNNO reduces and the crosslinking density. Three point bending test shows that when the PNNO is properly introduced, the formation of C-O bond has higher flexibility and conducive to the movement of molecular chains than C-N bond. It can enhance the material's toughness, but when the PNNO/DDM compound proportion reaches to a certain value, the mechanical properties of materials will reduce due to the compatibility. The LOI and UL-94 analysis show that, the introduction of PNNO can significantly improve flame retardant property of materials, with the V-0 grade of UL-94, non-dropping and 36 % of LOI.

(4) The influence of the introduction of DOPO-containing Schiff-base flame retardant (DPN) on the properties of DPN/EP curing system were analyzed. TGA results show that the carbon residue rate (700 ℃) can reach 30.9 % in the nitrogen. The T_g values of DPN/EP curing system arevery close to that of EP0,because there are four active H—N bonds in the molecular structure of DPN, and the reaction activity is similar to DDM, which results in a higher density of cross link. The values of

E-190 ℃ and tanδ also show that DPN can better participate in the curing of epoxy and lead to a high crosslinking density. The introduction of DPN can efficiently improve flame retardant property of materials, with the V-0 grade of UL-94, non-dropping and 41 % of LOI.

(5) The comparisons of the performances of PNOH/EP, PNNO/EP, DPN/EP show that the reaction activity of H—N bond is stronger than that of alcohol or phenol hydroxyl groups. With higher the functional group activity， greater degree of functionality and the concentration of the reactive activity, the degree of crosslinking will be greater. And the linear structure of the multi phenyl can also increase the tightness of the epoxy system and keep the T_g value high. The introduction of C—O bond is more conducive to the movement of molecular chains than C—N bond, and enhance toughness and stress of the material. At the same time, the linear structure of multi rigid benzene can increase the material rigidity and better deformation resistance force.The flame retardant properties of DOPO-containing Schiff-base flame retardant are better, because of its high content of P, N and the density distribution of the DOPO groups.

Key words: epoxy resin, flame retardant, Schiff-base compound.

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